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# INTERLABORATORY STUDY 90-7

# N-NITROSODIMETHYLAMINE IN INDUSTRIAL EFFLUENTS AND SEWAGE INFLUENT AND EFFLUENT

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# N-NITROSODIMETHYLAMINE IN INDUSTRIAL EFFLUENTS AND SEWAGE INFLUENT AND EFFLUENT

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## 1 SUMMARY AND CONCLUSIONS

The detection of N-nitrosodimethylamine (NDMA) in the drinking water supply of Elmira, Ontario occurred in 1989 during an open characterization scan. As this was an organic compound that had previously not been tested for under routine conditions, there quickly developed a need for an accurate and reliable method for the quantitative analysis of NDMA in various aqueous matrices. The Quality Management Unit of Environment Ontario's Laboratory Services Branch agreed to conduct several interlaboratory studies to assess the comparability of NDMA analytical procedures in water and wastewater.

A series of interlaboratory studies for the analysis of NDMA, conducted between March and July 1990, have been reported as Interlaboratory Study 90-2 (1). The results from those studies indicated that there was no clear consensus among the laboratories performing the analysis. Since the analytical procedures were being altered somewhat throughout these earlier studies, Study 90-7 was scheduled for November 1990 to reassess the sources of interlaboratory variability. The goals of the study were: to ascertain calibration agreement among laboratories analyzing NDMA, to ascertain the capability for correct identification, and to evaluate the impact of matrix on recovery, accuracy, and precision using different effluent matrices. Participants received a series of ampouled standards and a series of spiked effluent matrix samples.

The results from this study demonstrated that all but one of the participants had improved their within-laboratory precision for the analysis of NDMA. The differences among the laboratories are primarily derived from differences in calibration standards rather than from differences in instrumentation (High Resolution Mass Spectrometry (HRMS) versus Low Resolution Mass Spectrometry (LRMS)). Better agreement among the laboratories to the design value and interlaboratory median was obtained by calculating a correction factor based on the results for the ampouled standards and applying it to the results for the spiked samples. The need for better agreement in calibration standards among the laboratories was clearly indicated.

One of the laboratories did not show improvement in their results when the correction factor was applied. It was observed that this laboratory did not have a 1:1 ratio for the native versus deuterated NDMA in the ampouled standards. This factor was identified in Interlaboratory Study 90-2 (1) as critical to providing accurate results when the method of Isotope Dilution is used.

The results from this study also indicated that Low Resolution Mass Spectrometry (LRMS) may be acceptable for the analysis of NDMA when applied to a well-characterized effluent (i.e. confirmed by HRMS). However, for any new organic contaminant, or different effluent matrices, HRMS analysis for NDMA is strongly recommended to evaluate the risk for interference from matrix constituents.

## 2 INTRODUCTION

In 1989, Environment Ontario personnel detected the presence of N-nitrosodimethylamine (NDMA) in the drinking water supply of Elmira, Ontario (2) and later in the effluent of the municipal waste treatment plant. As NDMA is a suspected carcinogen (3,4), there was an immediate need for accurate and reliable monitoring of the various aqueous matrices for NDMA. Various government, industrial, and commercial laboratories developed analytical methods for the quantitative analysis of NDMA in drinking water and effluents. In early 1990, the Quality Management Unit (QMU) of Environment Ontario's Laboratory Services Branch (LSB) was asked to evaluate the comparability of data from these laboratories. A series of interlaboratory studies in reagent water and sewage influent were conducted and reported as Interlaboratory Study 90-2 (1). The results indicated that further method development was required by the participants and further interlaboratory studies were required to monitor improvements.

Interlaboratory Study 90-7 was designed with three goals. One was to ascertain the agreement in calibration among laboratories analyzing NDMA. A second goal was to ascertain the capability for correct identification by Gas Chromatography/High Resolution Mass Spectrometry (GC/HRMS), Gas Chromatography/Low Resolution Mass Spectrometry (GC/LRMS), and Gas Chromatography/Thermal Energy Analyzer (GC/TEA). The third goal was to evaluate recovery, accuracy and precision of NDMA analysis in several different effluent matrices. Participating laboratories received a set of 3 ampouled standards containing native and deuterated ($d_6$) NDMA for direct instrumental analysis to determine goal one. The participants also received twelve spiked matrix samples, three each of four different matrices, to assess the second and thrid goals. Nine laboratories participated in this study.

The following section describes the sample preparation, sample distribution and data handling techniques. The results are presented in Appendix I and are discussed in Section 4.

## 3 PROCEDURE

### 3.1 SAMPLE AND AMPOULE PREPARATION

The stock spiking solution was prepared from a concentrated NDMA solution of 97 µg/mL NDMA in ethanol. This solution, certified by the supplier is traceable to USDA Reference 7 Nitrosamine Standard, was obtained from Thermedics Inc., Woburn MA, Lot #322-69. A spiking solution for the matrix samples was prepared by diluting the concentrated stock solution in methanol. The volumetric flask containing the dilute solution was stored overnight in a freezer at -20°C. The solution was sealed into 5 mL amber ampoules the following day. The ampoules were stored at 4°C in the dark.

Forty litres each of four different effluent matrices were collected on November 14, 1990 in amber glass bottles. The matrices chosen were: Uniroyal Elmira Equalization Tank, Uniroyal Elmira Carboxin Tank, Elmira Sewage Treatment Plant Influent and Elmira Sewage Treatment Plant Effluent. Each separate matrix was homogenized in stainless steel tanks. Particulate matter in the Carboxin and STP Influent matrices was allowed to settle and formed a "cake" at the bottom of the tank. Prior to pouring into individual 1 litre amber bottles for distribution to the participants, the bulk samples were gently stirred to homogenize them. The 1 litre sample bottles were filled to the top with each matrix. Random weighing of the bottles before and after filling determined that each bottle held 1040 mL of each matrix.

Each participant received three samples of each matrix for a total of twelve samples. The samples were labelled as follows:

| | | | |
|---|---|---|---|
| Effluent 1 (Equalization Tank): | 1A | 1B | 1C |
| Effluent 2 (Carboxin Tank): | 2A | 2B | 2C |
| Effluent 3 (STP Influent): | 3A | 3B | 3C |
| Effluent 4 (STP Effluent): | 4A | 4B | 4C |

The "A" samples were not spiked ("Blank"). The spiking level for the "B" and "C" samples were designed to assess the analytical capability for the participants at the discharge limit of 0.500 µg/L of NDMA (5). Target levels were just below and just above this level. All spiking was done with the appropriate microlitre syringe. The design values are given in Table 1.

The ampouled standards for direct instrumental analysis were serially diluted from a concentrated stock solution. The stock solution was prepared from the following neat compounds: NDMA from Supelco Inc., Lot #LA03531 and $d_6$-NDMA from MSD Isotopes, Lot 4002-0. The stock solution was prepared in methanol and hand-sealed into 5 mL amber ampoules. Subsequent dilutions were prepared in dichloromethane and hand-sealed into 5 mL amber ampoules. Three levels were chosen to cover the normal calibration range. The ampoules were labelled NDMA STD 1 (low), NDMA STD 2 (mid-range), and NDMA STD 3 (high). The design values are given in Table 3.

## 3.2 SAMPLE DISTRIBUTION

The samples were cooled and packed in cardboard cartons lined with Styrofoam chips. The ampoules were placed in styrofoam holders and inserted into a box. The samples to the US participant were shipped by Purolator Courier on November 20, 1990. One commercial lab participant picked up its own sample set also on November 20. The remaining sample sets were delivered by LSB personnel on November 21, 1990.

All participants were provided with report forms for the results (Appendix 2). Participants were also requested to provide a copy of the chromatograms and ion traces with their results as well as a copy of their analytical procedure.

## 3.3 DATA HANDLING

All results were entered into an electronic spreadsheet. The mean, median, and standard deviation were calculated for each sample and are given in Table 1 of Appendix 1. In Table 2 the results for the spiked samples were also converted into percent recovery of the design value. For each matrix, the corresponding "A" value, as reported by each participant, was subtracted from the spiked "B" and "C" samples before calculating the percent recovery. The within-laboratory mean recovery and standard deviation were also calculated and are given in Table 2 of Appendix 1. The results for the ampouled standards are given in Table 3 of Appendix 1.

The results for the spiked samples ("B" and "C" samples) were plotted using the Youden two-sample technique (6). The laboratories were grouped according to instrumental type (ie. HRMS, LRMS or TEA). The results are plotted in Figures 1-3 in Appendix 1.

To assess the linearity of each participants results for the ampouled standards, the results were plotted versus the target value. The participants were again grouped according to instrument type. The results are shown in Figures 6 to 9 in Appendix 1.

A preliminary review of the plotted results in Figures 1 and 2 and of the ampouled standards showed that differences among laboratories appeared due to differences in calibration. To check this, a "correction factor" for each laboratory was calculated based on the ratio of reported NDMA to $d_6$-NDMA in the ampoules to the target ratio. The formula is as follows:

$$\text{correction factor} = \frac{(\text{Design NDMA} / \text{Design } d_6\text{-NDMA})}{(\text{Reported NDMA} / \text{Reported } d_6\text{-NDMA})}$$

This correction factor was calculated only for the participants using HRMS and LRMS, as the Thermal Energy Analyzer (TEA) technique does not use isotope dilution and does not distinguish between the native and deuterated NDMA. The correction factors are given in Table 3 of Appendix 1.

The reported sample results then had the correction factor applied and the percent recovery recalculated. These results are given in Tables 4 and 5 in Appendix 1. The results were again plotted using the Youden two-sample technique and are presented in Figures 4 and 5 in Appendix 1.

The participants were mailed a copy of the preliminary tables of results on December 21, 1990. The participants were invited to an interanalysts meeting on January 8, 1991, where the graphs and the data sets with the "correction factor" were presented. Items from this meeting are included in the discussion (Section 4).

## 4 RESULTS AND DISCUSSION

Results were received from all of the participants within the prescribed time-limits. Some participants were delayed in submitting their analytical methodology, so the meeting was in January 1991.

Laboratory 8002 did not report results for samples 1A, 1B, and 1C due to low recovery for $d_6$-NDMA and interferences. The results for samples 2A, 2B, 2C, 3A, 3B, 3C, and 4A were all qualified by the letter "i", indicating interference.

Laboratory 8003 qualified their result for sample 3A with an "i", indicating interference.

Laboratory 8004 reported their data within the prescribed timeframe using a new instrument. When they received the preliminary tables of results, they were concerned about their lack of agreement with the other participants. Investigation with their new instrument led to the discovery of several software problems. They reanalyzed the sample extracts and submitted an additional set of results in January 1991. These results are listed in Table 1 but are not included in the statistical calculations.

Laboratory 8007 requested a duplicate set of samples and analyzed them using two different instrumental techniques. The set analyzed using GC/LRMS is identified as 8007A and the set analyzed using GC/TEA is identified as 8007B.

The results in Figure 1 demonstrate good within-laboratory precision for the participants using HRMS (Laboratories 8001, 8004 and 8006). Matrix effects appear to be minimized using this technique, as results from the different matrices are clustered together. The results from the participants using LRMS (Laboratories 8002, 8003, 8007A, 8008, and 8009) also demonstrate good within-laboratory precision, except for Laboratory 8008 (Figure 2). Laboratories using GC/TEA demonstrated variable performance, with Laboratory 8007B demonstrating good within-laboratory precision and Laboratory 8005 demonstrating variable within-laboratory performance using the same technique (Figure 3).

As the different matrices do not appear to present any problems for the analyses, the differences among the laboratories appear to be due to differences in standards. The ampouled standards provided for direct analysis were designed to cover the normal analytical working range. The results as plotted in Figures 6-9 demonstrate that the calibration curves of the participants differ. Of the laboratories using HRMS, Laboratory 8001's results for the standards were the closest to the design value and their results for the spiked samples were also the closest to the design value. Similarly, for the laboratories using LRMS, Laboratory 8003's results for the standards and spiked samples were both the closest to the design values. The low results for the standards as reported by Laboratory 8005 appears related to the low results for the spiked samples, as compared to Laboratory 8007B, the other laboratory using TEA.

To assess the difference among the laboratories based on the differences in the standards, a correction factor was calculated using the procedure described in Section 3.3. The results for STD3 were chosen as they are closest to the NDMA levels found in the spiked samples used in this study. This technique was applied to the results for the laboratories using HRMS and LRMS only.

Figure 4 for the laboratories using HRMS show the results for two of the laboratories moving much closer to the design value and the interlaboratory median. Laboratory 8004 did not have close to a 1:1 ratio for STD3, resulting in their "correction factor" moving their results further away from the design value. As noted above, software problems with their new instrument contributed to the incorrect analyses of the NDMA standards in this study but they believe the problems have been corrected for future studies.

Figure 5 for the laboratories using LRMS also shows some improvement in the spread of results among the laboratories. The results for 4 of the 5 laboratories are generally closer to the design value and interlaboratory median. Unfortunately the "correction factor" does not appear to significantly improve the performance of Laboratory 8008, possibly due to the greater within-laboratory variability as noted above.

This overall improvement demonstrated by the application of the correction factor shows that the major difference among the participants may be attributed to a difference in their calibration standards or possibly a difference in their calibration techniques. A review of their procedures provided with the results indicated that some laboratories used a three-point calibration and some laboratories used a one-point calibration. The level of the standard used for a one-point calibration would have to be chosen very carefully to minimize the effects of curvature. It may have to be adjusted according to the levels of NDMA present in the samples being analyzed. While the results from this study do not indicate significant curvature by any of the participants, it is recommended that calibration control be carefully maintained by all laboratories performing NDMA analysis.

The use of various instrumental detectors for NDMA analysis, HRMS, LRMS or TEA, has been a source of difference among laboratories. Interlaboratory Study 90-2 (1) demonstrated that HRMS produced reliable and accurate results, LRMS was not as reliable on unknowns or low levels, and TEA was even less reliable for unknowns and not capable of detecting low levels of NDMA. The results from this study show that for a well characterized effluent/influent matrix, such as the matrices used for this study, LRMS may produce reliable and accurate results (7). However for matrices that are not well characterized, HRMS is the more reliable technique.

The results for this interlaboratory study for NDMA analysis have shown marked improvement to previous studies (1). It is the intent of Laboratory Services Branch QM Unit to continue to conduct interlaboratory studies for the analysis of NDMA in a variety of different effluent and drinking water matrices.

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## 6 APPENDIX I: TABLES AND GRAPHS

Table 1 Results of Spiked Samples in ppb (µg/L)

Table 2 Results of Samples Converted to Percent Recovery

Table 3 Results of Ampouled Standards in pg/µL

Table 4 Results of Spiked Samples Corrected using CORRECTION FACTOR; Results in ppb (µg/L)

Table 5 Results of Samples Corrected Using CORRECTION FACTOR and Converted to Percent Recovery

Figure 1 Youden Plot of Laboratories using HRMS

Figure 2 Youden Plot of Laboratories using LRMS

Figure 3 Youden Plot of Laboratories using TEA

Figure 4 Youden Plot of Laboratories using HRMS after CORRECTION FACTOR applied

Figure 5 Youden Plot of Laboratories using LRMS after CORRECTION FACTOR applied

Figures 6-9 Plots of Results of Ampouled Standards vs. Design Value

# TABLE 1 - INTERLABORATORY STUDY 90-7
## Results in ppb (μg/L)

| MATRIX | EQUALIZATION TANK | | | CARBOXIN TANK | | | STP INFLUENT | | | STP EFFLUENT | | | INST. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAMPLE | 1A | 1B | 1C | 2A | 2B | 2C | 3A | 3B | 3C | 4A | 4B | 4C | |
| ID CODE | | | | | | | | | | | | | |
| DESIGN | | 0.384 | 0.59 | | 0.384 | 0.59 | | 0.384 | 0.59 | | 0.384 | 0.59 | |
| 8001 | 0.077 | 0.41 | 0.65 | 0.042 | 0.4 | 0.63 | 0.038 | 0.36 | 0.63 | 0.021 | 0.33 | 0.59 | HRMS |
| 8002 | NOT REPORTED | | | 0.0584i | 0.4306i | 0.6592i | 0.1024i | 0.3708i | 0.567i | 0.0265i | 0.3355 | 0.6314 | LRMS |
| 8003 | 0.036 | 0.43 | 0.664 | 0.049 | 0.459 | 0.684 | 0.028i | 0.381 | 0.538 | 0.023 | 0.434 | 0.642 | LRMS |
| 8004 | 0.0704 | 0.585 | 0.792 | 0.0322 | 0.554 | 0.743 | 0.0357 | 0.488 | 0.744 | 0.0179 | 0.571 | 0.737 | HRMS |
| 8005 | 0.064 | 0.54 | 0.482 | 0.055 | 0.36 | 0.471 | <.02 | 0.32 | 0.55 | <.02 | 0.4 | 0.426 | TEA |
| 8006 | 0.068 | 0.479 | 0.874 | 0.048 | 0.427 | 0.748 | 0.034 | 0.467 | 0.671 | 0.014 | 0.462 | 0.581 | HRMS |
| | | | 0.733 | | | | | 0.414 | | 0.016 | 0.415 | | |
| 8007A | 0.0735 | 0.474 | 0.717 | 0.059 | 0.428 | 0.652 | 0.035 | 0.442 | 0.644 | ND | 0.461 | 0.645 | LRMS |
| 8007B | 0.0925 | 0.472 | 0.734 | 0.0635 | 0.459 | 0.653 | 0.036 | 0.431 | 0.64 | ND | 0.469 | 0.623 | TEA |
| 8008 | 0.0377 | 0.453 | 0.675 | 0.0241 | 0.458 | 0.691 | 0.0857 | 0.387 | 0.689 | 0.098 | 0.35 | 0.632 | LRMS |
| 8009 | 0.055 | 0.345 | 0.5 | 0.065 | 0.335 | 0.475 | 0.05 | 0.325 | 0.485 | 0.04 | 0.3 | 0.44 | LRMS |
| MEAN | 0.0638 | 0.4188 | 0.6821 | 0.0496 | 0.4311 | 0.6406 | 0.0445 | 0.3987 | 0.6158 | 0.0233 | 0.4116 | 0.5947 | |
| MEDIAN | 0.068 | 0.472 | 0.696 | 0.052 | 0.4293 | 0.6561 | 0.0359 | 0.387 | 0.635 | 0.0179 | 0.415 | 0.6272 | |
| STD DEV | 0.0183 | 0.1613 | 0.1202 | 0.0135 | 0.0603 | 0.0963 | 0.0293 | 0.0549 | 0.0791 | 0.0277 | 0.0794 | 0.0950 | |
| MED.-MED.BLK | | 0.404 | 0.628 | | 0.3773 | 0.6041 | | 0.3511 | 0.5991 | | 0.3971 | 0.6093 | |
| 8004 * | 0.081 | 0.396 | 0.618 | 0.072 | 0.354 | 0.619 | 0.038 | 0.413 | 0.624 | 0.015 | 0.364 | 0.620 | |

* Second data set reported after review of original results. Not included in statistical calculations.

# TABLE 2 - INTERLABORATORY STUDY 90-7
## Results as Percent Recovery of Design Value ("Background Corrected")

| MATRIX | EQUALIZATION TANK | | CARBOXIN TANK | | STP INFLUENT | | STP EFFLUENT | | WITHIN LABORATORY MEAN RECOVERY | WITHIN LABORATORY RELATIVE STD DEV | INST. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **SAMPLE** | **1B** | **1C** | **2B** | **2C** | **3B** | **3C** | **4B** | **4C** | | | |
| **DESIGN** | 0.3840 | 0.5900 | 0.3840 | 0.5900 | 0.3840 | 0.5900 | 0.3840 | 0.5900 | | | |
| **ID CODE** | | | | | | | | | | | |
| **8001** | 86.7% | 97.1% | 93.2% | 99.7% | 83.9% | 100.3% | 80.5% | 96.4% | 92.2% | 7.6% | HRMS |
| **8002** | | | 96.9% | 101.8% | 69.9% | 78.7% | 80.5% | 102.5% | 88.4% | 13.8% | LRMS |
| **8003** | 102.6% | 106.4% | 106.8% | 107.6% | 91.9% | 86.4% | 107.0% | 104.9% | 101.7% | 8.0% | LRMS |
| **8004** | 134.0% | 122.3% | 135.9% | 120.5% | 117.8% | 120.1% | 144.0% | 121.9% | 127.1% | 9.6% | HRMS |
| **8005** | 124.0% | 70.8% | 79.4% | 70.5% | 83.3% | 93.2% | 104.2% | 72.2% | 87.2% | 19.0% | TEA |
| **8006** | 107.0% | 136.6% | 98.7% | 118.6% | 112.8% | 108.0% | 116.7% | 96.1% | 81.3% | 11.7% | HRMS |
| | | 124.2% | | | 107.8% | | 103.9% | | | | |
| **8007A** | 104.3% | 109.1% | 96.1% | 100.5% | 106.0% | 103.2% | 120.1% | 109.3% | 106.1% | 7.1% | LRMS |
| **8007B** | 98.8% | 108.7% | 103.0% | 99.9% | 102.9% | 102.4% | 122.1% | 105.6% | 105.4% | 7.4% | TEA |
| **8008** | 108.2% | 108.0% | 113.0% | 113.0% | 78.5% | 102.3% | 65.6% | 90.5% | 97.4% | 17.5% | LRMS |
| **8009** | 75.5% | 75.4% | 70.3% | 69.5% | 71.6% | 73.7% | 67.7% | 67.8% | 71.4% | 3.2% | LRMS |
| **MEAN** | 104.6% | 105.9% | 99.3% | 100.2% | 93.3% | 96.8% | 101.1% | 96.7% | | | |
| **MEDIAN** | 104.3% | 108.4% | 97.8% | 101.2% | 87.9% | 101.3% | 104.0% | 99.5% | | | |
| **STD DEV** | 19.5% | 19.7% | 19.9% | 17.3% | 16.7% | 14.9% | 24.4% | 17.0% | | | |
| **8004 *** | 85.2% | 92.1% | 77.6% | 93.5% | 97.9% | 99.4% | 91.2% | 102.6% | 92.4% | 8.1% | HRMS |

* Second data set reported after review of original results. Not included in statistical calculations.

Background corrected: For Samples "B" and "C", the result for the corresponding "A" sample has been subtracted before calculating the percent recovery relative to the design value.

## TABLE 3 - INTERLABORATORY STUDY 90-7
NDMA Standard Ampoules; Results in pg/μL

| | NDMA STD1 | | NDMA STD2 | | NDMA STD3 | | RATIO - NATIVE: DEUTERATED | CORRECTION FACTOR | INST. |
|---|---|---|---|---|---|---|---|---|---|
| ID CODE | NATIVE | DEUTERATED | NATIVE | DEUTERATED | NATIVE | DEUTERATED | | | |
| DESIGN | 2.5 | 2.6 | 25.3 | 26 | 253 | 260 | 0.9731 | | |
| 8001 | 2.24 | 3.01 | 20.4 | 21 | 242 | 267 | 0.9064 | 1.0736 | HRMS |
| 8002 | - | - | 17.471 | 17.242 | 238.486 | 251.918 | 0.9467 | 1.0279 | LRMS |
| 8003 | 2 | 2 | 25 | 27 | 256 | 281 | 0.9110 | 1.0681 | LRMS |
| 8004 | 1.9 | 1.44 | 23.8 | 17.4 | 199 | 89 | 2.2360 | 0.4352 | HRMS |
| 8006 | 2.846 | 2.19 | 32.567 | 30.586 | 290.72 | 276.16 | 1.0527 | 0.9243 | HRMS |
| 8007A | ND | ND | 26.944 | 25.777 | 296 | 303.023 | 0.9768 | 0.9962 | LRMS |
| 8008 | <10 | <10 | 12.9 | 16.7 | 234 | 280 | 0.8357 | 1.1644 | LRMS |
| 8009 | <10 | <10 | 20 | 20 | 225 | 260 | 0.8654 | 1.1244 | LRMS |

## TABLE 4 - INTERLABORATORY STUDY 90-7

### Results Corrected using CORRECTION FACTOR from Ampoules; Results in ppb (µg/L)

| MATRIX | EQUALIZATION TANK | | | CARBOXIN TANK | | | STP INFLUENT | | | STP EFFLUENT | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAMPLE | 1A | 1B | 1C | 2A | 2B | 2C | 3A | 3B | 3C | 4A | 4B | 4C | INSTR. |
| ID CODE | | | | | | | | | | | | | |
| DESIGN | | 0.3840 | 0.5900 | | 0.3840 | 0.5900 | | 0.3840 | 0.5900 | | 0.3840 | 0.5900 | |
| 8001 | 0.0827 | 0.4402 | 0.6978 | 0.0451 | 0.4294 | 0.6764 | 0.0408 | 0.3865 | 0.6764 | 0.0225 | 0.3543 | 0.6334 | HRMS |
| 8002 | | | | 0.0600 | 0.4426 | 0.6776 | 0.1053 | 0.3811 | 0.5828 | 0.0272 | 0.3449 | 0.6490 | LRMS |
| 8003 | 0.0385 | 0.4593 | 0.7092 | 0.0423 | 0.4903 | 0.7306 | 0.0299 | 0.4069 | 0.5746 | 0.0246 | 0.4636 | 0.6857 | LRMS |
| 8004 | 0.0306 | 0.2546 | 0.3447 | 0.0140 | 0.2411 | 0.3234 | 0.0155 | 0.2124 | 0.3238 | 0.0078 | 0.2485 | 0.3207 | HRMS |
| 8006 | 0.0629 | 0.4427 | 0.8078 | 0.0444 | 0.3947 | 0.6914 | 0.0314 | 0.4316 | 0.6202 | 0.0129 | 0.4270 | 0.5370 | HRMS |
| | | | 0.6775 | | | | | 0.3827 | | 0.0148 | 0.3836 | | |
| 8007A | 0.0732 | 0.4722 | 0.7143 | 0.0588 | 0.4264 | 0.6495 | 0.0349 | 0.4403 | 0.6416 | 0.0000 | 0.4592 | 0.6425 | LRMS |
| 8008 | 0.0439 | 0.5275 | 0.7860 | 0.0281 | 0.5333 | 0.8046 | 0.0998 | 0.4506 | 0.8023 | 0.1141 | 0.4075 | 0.7359 | LRMS |
| 8009 | 0.0618 | 0.3879 | 0.5622 | 0.0731 | 0.3767 | 0.5341 | 0.0562 | 0.3654 | 0.5453 | 0.0450 | 0.3373 | 0.4947 | LRMS |
| MEAN | 0.0562 | 0.4263 | 0.6624 | 0.0457 | 0.4168 | 0.6360 | 0.0517 | 0.3842 | 0.5959 | 0.0299 | 0.3807 | 0.5874 | |
| MEDIAN | 0.0618 | 0.4415 | 0.6978 | 0.0448 | 0.4264 | 0.6764 | 0.0379 | 0.3853 | 0.5900 | 0.0225 | 0.3838 | 0.6334 | |
| STD DEV | 0.0191 | 0.0865 | 0.1482 | 0.0187 | 0.0869 | 0.1474 | 0.0331 | 0.0709 | 0.1357 | 0.0341 | 0.0682 | 0.1325 | |

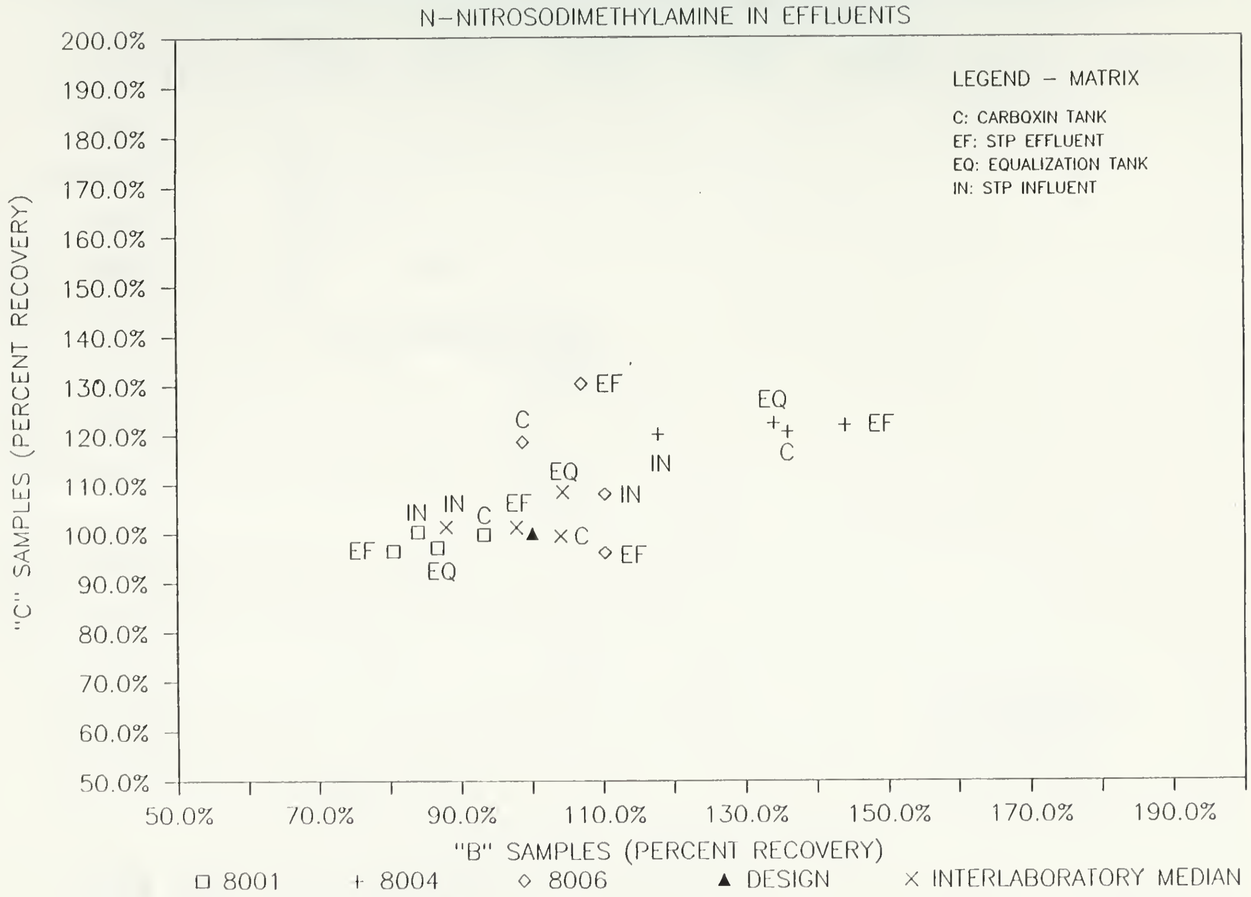
## TABLE 5 - INTERLABORATORY STUDY 90-7

## Results Corrected using CORRECTION FACTOR Expressed as Percent Recovery ("Background Corrected")

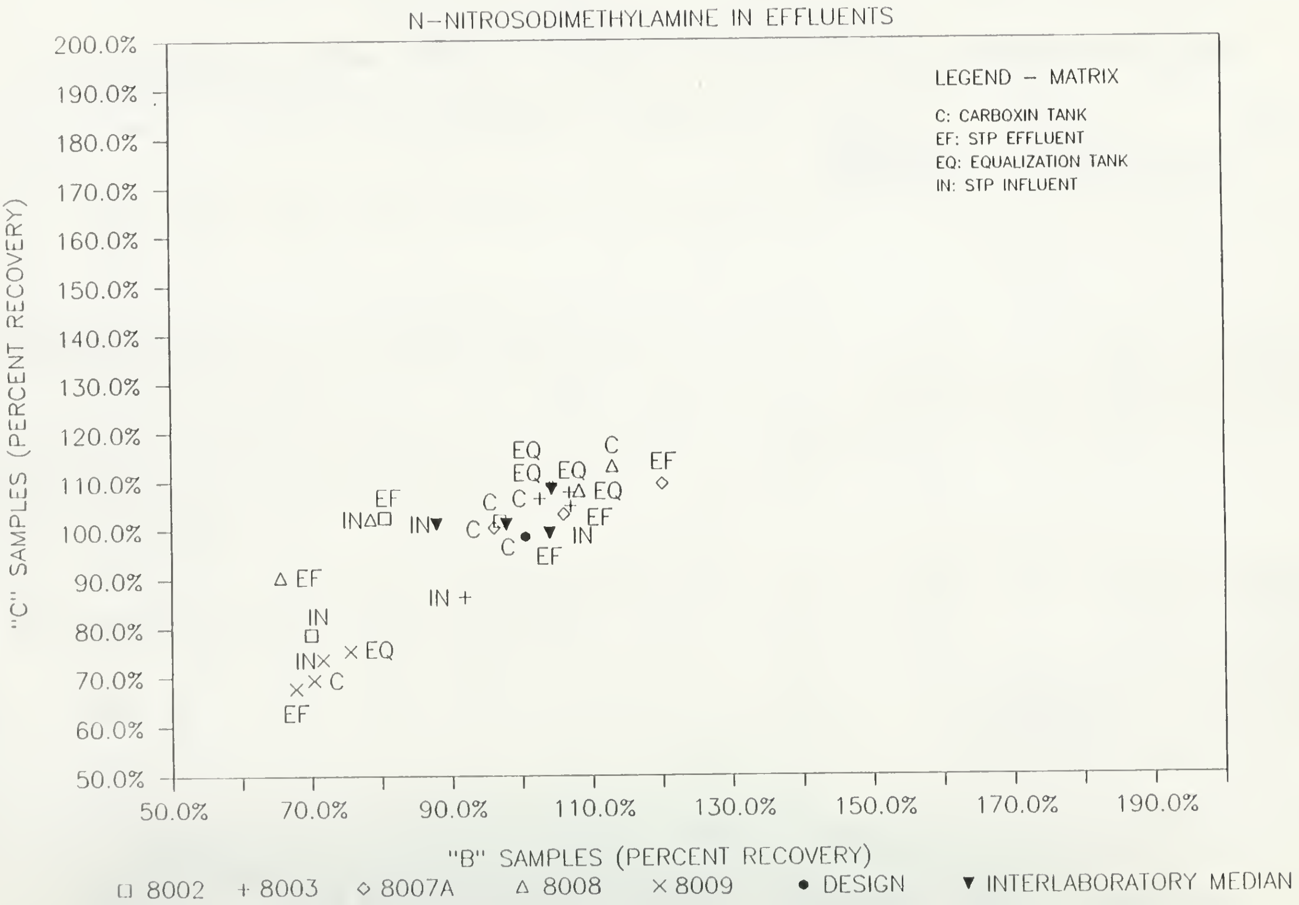
| MATRIX | EQUALIZATION TANK | | CARBOXIN TANK | | STP INFLUENT | | STP EFFLUENT | | WITHIN-LABORATORY MEAN RECOVERY | WITHIN-LABORATORY RELATIVE STD DEV | INST. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SAMPLE | 1B | 1C | 2B | 2C | 3B | 3C | 4B | 4C | | | |
| | | | | | | | | | | | |
| DESIGN | 0.3840 | 0.5900 | 0.3840 | 0.5900 | 0.3840 | 0.5900 | 0.3840 | 0.5900 | | | |
| 8001 | 93.1% | 104.3% | 100.1% | 107.0% | 90.0% | 107.7% | 86.4% | 103.5% | 99.0% | 8.1% | HRMS |
| 8002 | | | 99.6% | 104.7% | 71.8% | 80.9% | 82.7% | 105.4% | 90.9% | 14.2% | LRMS |
| 8003 | 109.6% | 113.7% | 114.0% | 115.0% | 98.2% | 92.3% | 114.3% | 112.1% | 108.6% | 8.6% | LRMS |
| 8004 | 58.3% | 53.2% | 59.1% | 52.4% | 51.3% | 52.2% | 62.7% | 53.0% | 55.3% | 4.2% | HRMS |
| 8006 | 98.9% | 126.3% | 91.2% | 109.7% | 104.2% | 99.8% | 107.6% | 88.7% | 103.4% | 10.8% | HRMS |
| | | 114.8% | | | 99.7% | | 96.3% | | | | |
| 8007A | 103.9% | 108.7% | 95.7% | 100.1% | 105.6% | 102.8% | 119.6% | 108.9% | 105.7% | 7.1% | LRMS |
| 8008 | 125.9% | 125.8% | 131.6% | 131.6% | 91.4% | 119.1% | 76.4% | 105.4% | 113.4% | 20.4% | LRMS |
| 8009 | 84.9% | 84.8% | 79.1% | 78.1% | 80.5% | 82.9% | 76.1% | 76.2% | 80.3% | 3.6% | LRMS |
| MEAN | 96.4% | 103.9% | 96.3% | 99.8% | 88.1% | 92.2% | 91.3% | 94.2% | | | |
| MEDIAN | 98.9% | 111.2% | 97.7% | 105.9% | 91.4% | 96.1% | 86.4% | 104.5% | | | |
| STD DEV | 21.2% | 24.3% | 21.7% | 24.3% | 17.7% | 20.5% | 19.3% | 20.4% | | | |

Background corrected: For Samples "B" and "C", the result for the corresponding "A" sample has been subtracted before calculating the percent recovery relative to the design value.

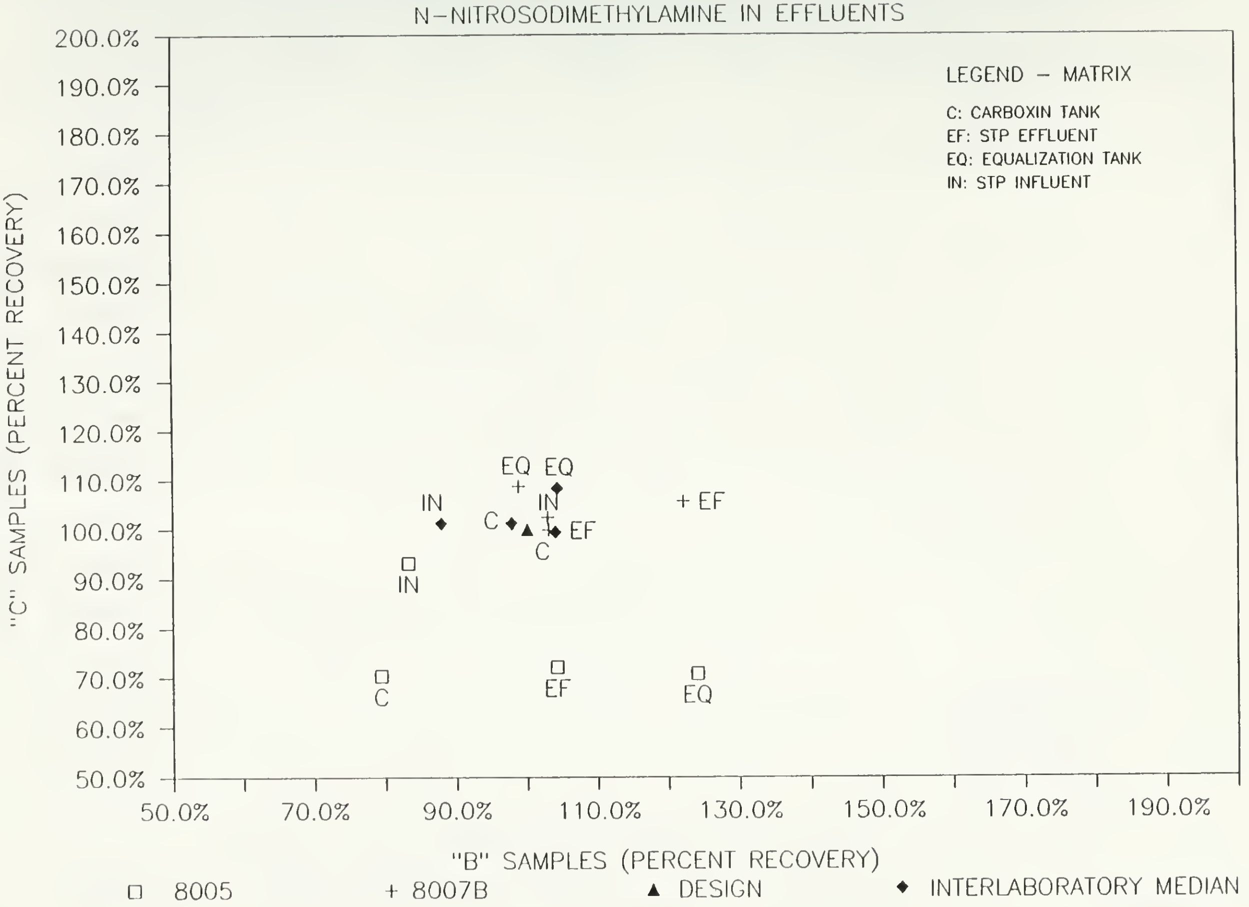
# FIG 1: INTERLABORATORY STUDY 90–7 HRMS



# FIG 2: INTERLABORATORY STUDY 90–7 LRMS

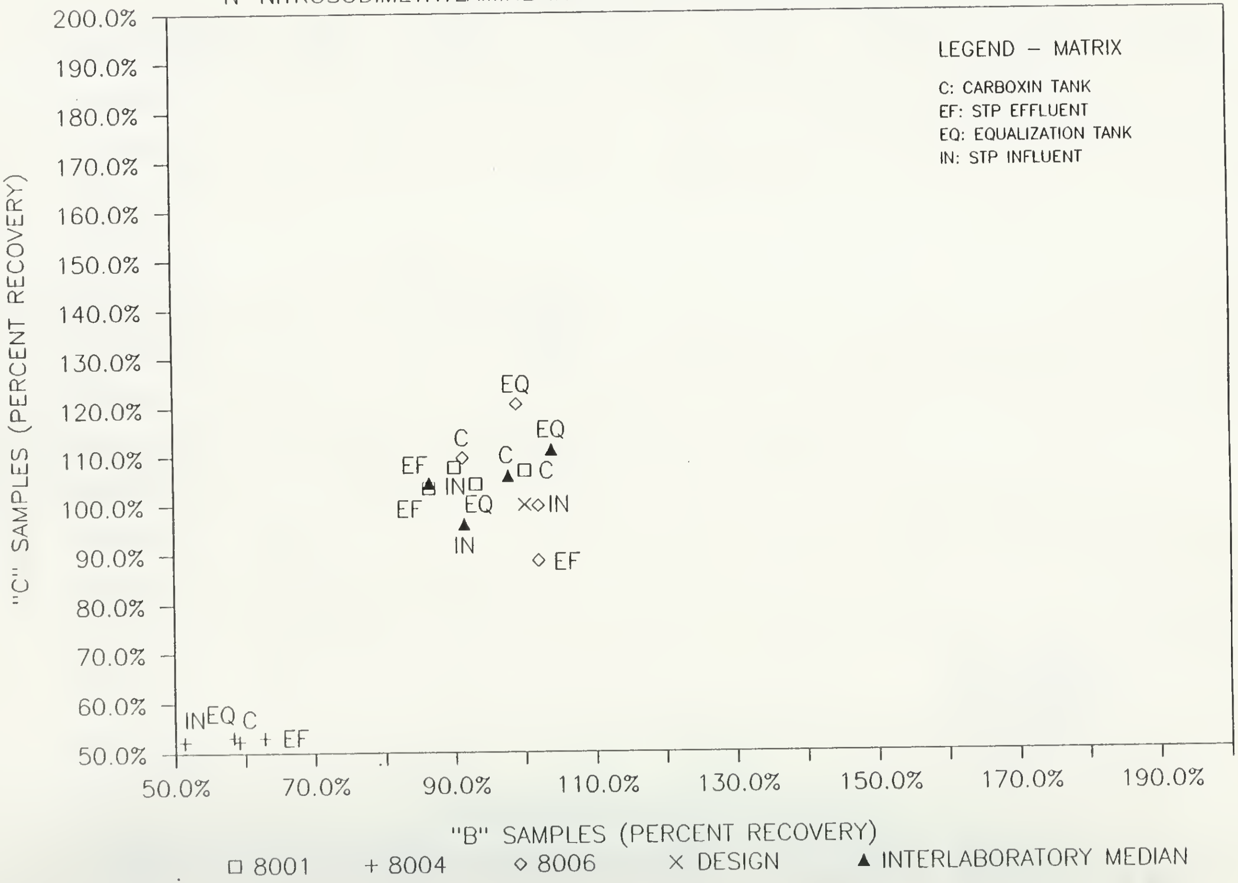


# FIG 3: INTERLABORATORY STUDY 90-7 TEA



# FIG 4: INTERLABORATORY STUDY 90-7 HRMS

N-NITROSODIMETHYLAMINE IN EFFLUENTS: CORRECTION FACTOR APPLIED



# FIG 5: INTERLABORATORY STUDY 90-7 LRMS

N-NITROSODIMETHYLAMINE IN EFFLUENTS: CORRECTION FACTOR APPLIED

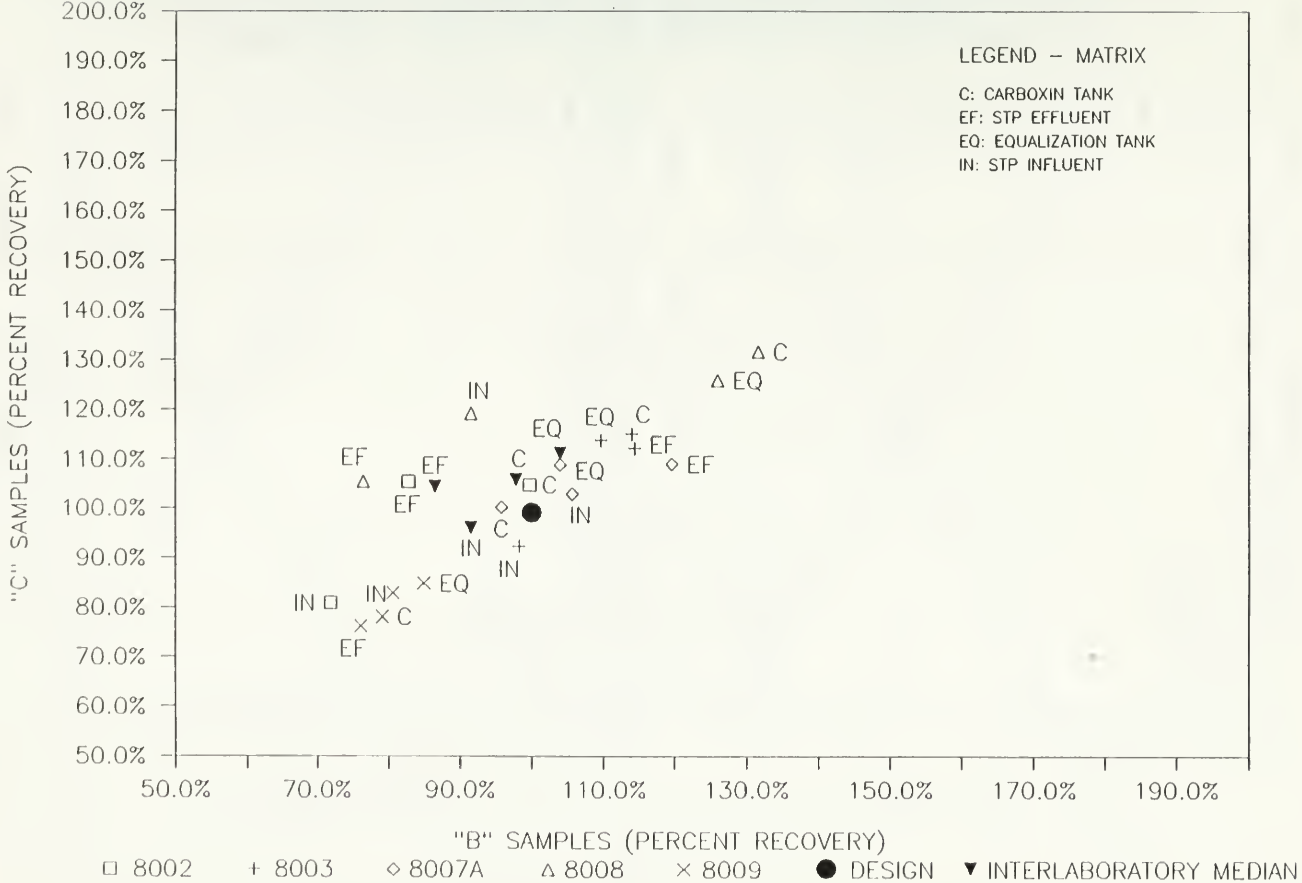


FIG 6: INTERLABORATORY STUDY 90-7: HRMS

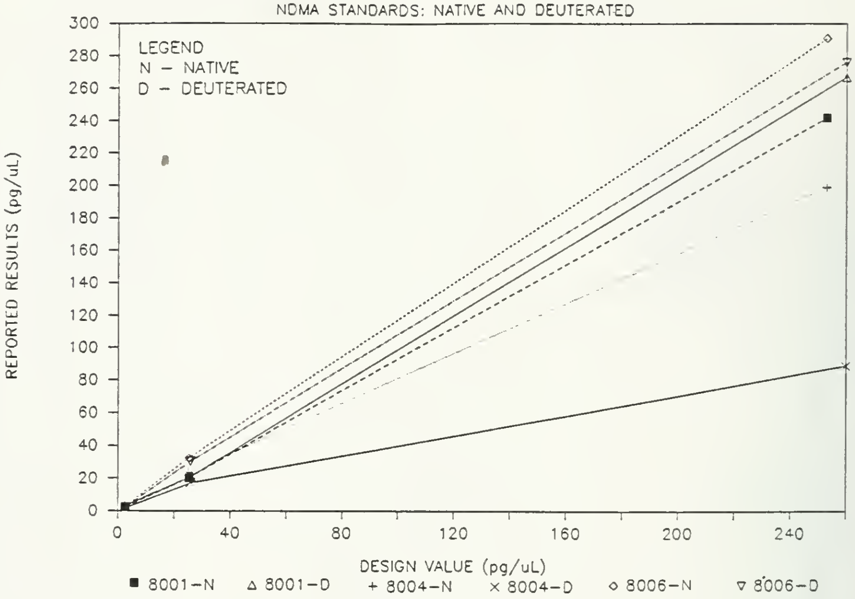
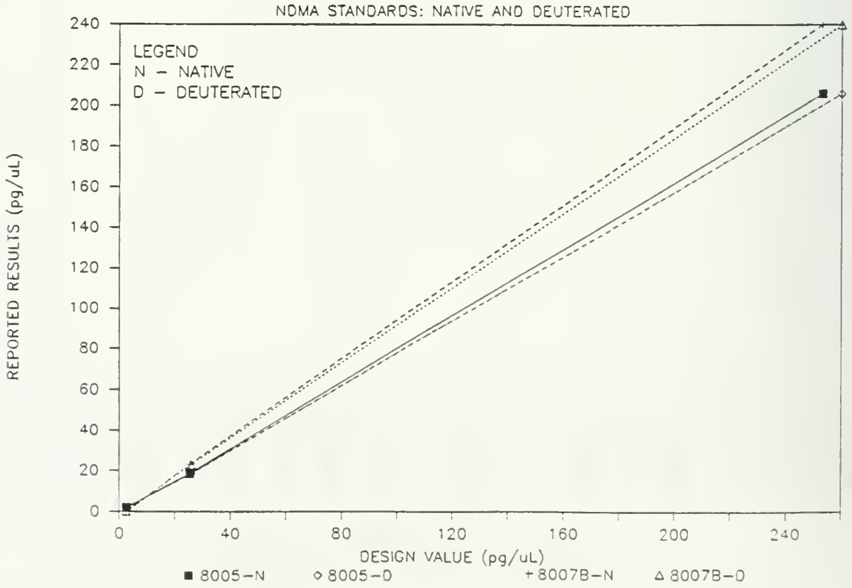
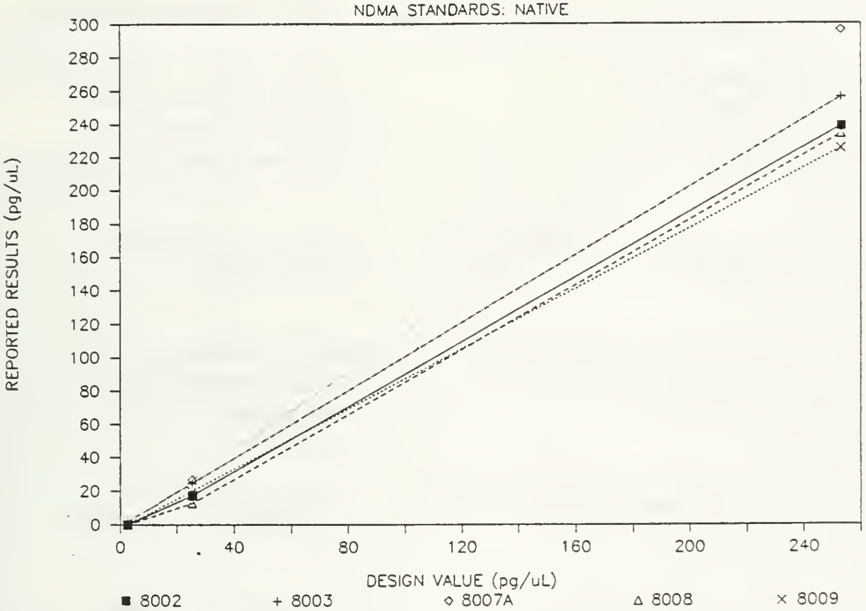


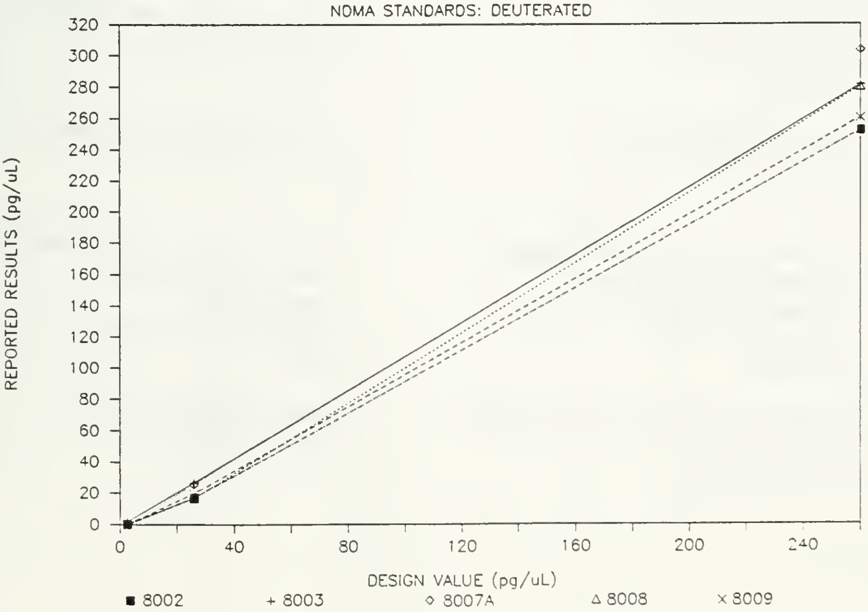
FIG 7: INTERLABORATORY STUDY 90-7: TEA



# FIG 8: INTERLABORATORY STUDY 90-7: LRMS



# FIG 9: INTERLABORATORY STUDY 90-7: LRMS



## 7 APPENDIX 2: LIST OF PARTICIPANTS AND CORRESPONDENCE

Uniroyal Chemical Ltd.
Research Laboratories
120 Huron St.
Guelph, Ontario
N1H 6N3

Contact: Paul Thomson/Anthony Riggs
(519) 822-3790

Canviro Analytical Laboratories Ltd.
50 Bathurst Dr., Unit 12
Waterloo, Ontario
N2V 2C5

Contact: Dale Sutherland/Annette Bibaud
(519) 747-2575

Environment Ontario
Laboratory Services Branch
Organic Water Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

Contact: C. David Hall
(416) 235-5910

Regional Municipality of Waterloo
Engineering Laboratory
100 Maple Grove Rd., R.R. #31
Cambridge, Ontario
N3H 3R6

Contact: Fizal Haniff/David Andrews
(519) 885-9500

Environment Ontario
Laboratory Services Branch
Mass Spectrometry Unit
125 Resources Rd.
Rexdale, Ontario, M9W 5L1

Contact: Vince Taguchi
(416)235-5902

Ortech International
2395 Speakman Dr.
Mississauga, Ontario
L5K 1B3

Contact: Jack Brady
(416) 822-4111, ext. 419

Environment Canada
Wastewater Technology Centre
Conservation and Protection
867 Lakeshore Rd., Box 5050
Burlington, Ontario
L7R 4A6

Contact: Robert Hong-You
(416) 336-44504

Uniroyal Chemical Company, Inc.
World Headquarters
Benson Road
Middlebury, CT 06749
U.S.A.

Contact: Albert Nitowski
(203) 573-3495

Eli-ECO Logic International
143 Dennis St.
Rockwood, Ontario
N0B 2K0

Contact: Elizabeth Chisholm
(519) 856-9591

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario, M9W 5L1
(416) 235-5842
FAX (416) 235-5744

November 14, 1990

## NOTIFICATION OF INTERLABORATORY STUDY 90-7: N-NITROSODIMETHYLAMINE IN EFFLUENTS PLUS CALIBRATION STANDARDS

The Quality Management Unit of the Laboratory Services Branch will be conducting a comprehensive interlaboratory variability study for the analysis of N-Nitrosodimethylamine. This study is to be conducted the week of November 26, 1990. Participating laboratories will receive three (3) ampoules of injection-ready calibration standards, consisting of native N-Nitrosodimethylamine and deuterated N-Nitrosodimethylamine, and twelve (12) samples of spiked influent and effluent. Analysis must be initiated within four days of receipt of samples. Results are to be reported by December 12, 1990, and must include a copy of the participant's official method for the analysis of N-Nitrosodimethylamine. (NOTE: The method must describe the procedures used in full detail and not be a summary of their own or MOE's method.)

All participants who reported results will be invited to attend an interanalysts meeting, tentatively scheduled for December 18, 1990 at 10:00 am at Environment Ontario, Laboratory Services Branch, 125 Resources Rd., Rexdale. The analysts meeting will occur if all the analysts participate in this interlaboratory study, and if full methodology is forwarded with the study results by December 12, 1990. The meeting will be delayed if this material has not been provided. The results will be summarized and presented at this meeting, as well as a comparison of the different methods used. A discussion period will allow for all participants to comment on the findings.

Laboratories receiving this notification must respond with the accompanying form by no later than November 21, 1990.

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX: (416) 235-5744

# MOE INTERLABORATORY VARIABILITY STUDY NOTIFICATION FOR THE ANALYSIS OF N-NITROSODIMETHYLAMINE

## STUDY 90-7

| | YES | NO |
|---|---|---|
| We will participate in MOE study 90-7 for the analysis of N-Nitrosodimethylamine. | ☐ | ☐ |

Minimum amount of sample volume required: ____________________

For the completeness of our records, and to avoid any shipping delays, please fill in the following:

| Mailing Address: | Shipping Address: |
|---|---|
| ____________________ | ____________________ |
| ____________________ | ____________________ |
| ____________________ | ____________________ |
| ____________________ | ____________________ |

Contact Person: ____________________________________________

Telephone: ____________________________________________

Please return this response form by November 21, 1990 to:

Sylvia Cussion
Environment Ontario
Laboratory Services Branch
Quality Management Unit
125 Resources Rd., P.O. Box 213
Rexdale, Ontario, M9W 5L1

(416) 235-5842
FAX: (416) 235-5744

Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

November 27, 1990

**TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-7**

Please find enclosed twelve (12) 1000 mL amber glass bottles plus three (3) 5 Ml amber ampoules. If you are missing any of the above samples or they have been broken in transit, please contact me at the above phone number immediately.

The twelve samples are to be analyzed for N-Nitrosodimethylamine (NDMA). They are labelled as follows:

| | | | |
|---|---|---|---|
| Effluent 1: | 1A | 1B | 1C |
| Effluent 2: | 2A | 2B | 2C |
| Effluent 3: | 3A | 3B | 3C |
| Effluent 4: | 4A | 4B | 4C |

Analysis of the samples must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 ±2 degrees Celcius **in the dark** until ready for analysis. A report form is attached. To assist in the accurate analysis of these samples, the expected level of NDMA in these samples is as follows:

For all "A" samples: <100 ppt NDMA
For all "B" samples: 300-500 ppt NDMA
for all "C" samples: 500-700 ppt NDMA

The ampoules are pure NDMA standards containing native and deuterated NDMA in dichloromethane. They are to be analyzed by direct injection and the results reported on the attached form. The ampoules are labelled as follows:

| | | | |
|---|---|---|---|
| Ampoules: | NDMA STD 1 | NDMA STD 2 | NDMA STD 3 |

To ensure that the timing of the analysts meeting is not delayed, results of the twelve samples and three ampoules are to be submitted by December 12, 1990. A report form is included with your lab identification number and the sample numbers described above. Also to be included with the results is a copy of the official method used by the participant for the analysis of N-Nitrosodimethylamine. This information will be kept confidential for the interanalysts meeting, with summaries of the differences in procedures being tabulated for discussion purposes.

Please note that there are three different report forms for the effluent samples. Please use the form appropriate to the instrumentation you used and supply the additional information requested. There is only one form for reporting the results from the ampoules. If possible, please also include a copy of the ion traces for each of the analyses.

Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

# INTERLABORATORY STUDY 90-7: NDMA

NOVEMBER 27, 1990

REPORT DUE DATE: DECEMBER 12, 1990

IDENTIFICATION CODE:

INSTRUMENTATION: GC/HRMS
LOCKMASS OR REFERENCE COMPOUND (including exact mass):

CONCENTRATION OF INTERNAL STANDARD (d6 NDMA):

| SAMPLE | RESULT (ng/L) | EXTRACTION VOLUME | FINAL VOLUME OF EXTRACT | INJECTION VOLUME | d6 SPIKE LEVEL | ION RATIO |
|---|---|---|---|---|---|---|
| 1A | | | | | | |
| 1B | | | | | | |
| 1C | | | | | | |
| 2A | | | | | | |
| 2B | | | | | | |
| 2C | | | | | | |
| 3A | | | | | | |
| 3B | | | | | | |
| 3C | | | | | | |
| 4A | | | | | | |
| 4B | | | | | | |
| 4C | | | | | | |

# INTERLABORATORY STUDY 90-7: NDMA

NOVEMBER 27, 1990

REPORT DUE DATE: DECEMBER 12, 1990

IDENTIFICATION CODE:

INSTRUMENTATION: GC/LRMS
LOCKMASS OR REFERENCE COMPOUND (including exact mass):

CONCENTRATION OF INTERNAL STANDARD (d6 NDMA):

| SAMPLE | RESULT (ng/L) | EXTRACTION VOLUME | FINAL VOLUME OF EXTRACT | INJECTION VOLUME | d6 SPIKE LEVEL | ION RATIO |
|---|---|---|---|---|---|---|
| 1A | | | | | | |
| 1B | | | | | | |
| 1C | | | | | | |
| 2A | | | | | | |
| 2B | | | | | | |
| 2C | | | | | | |
| 3A | | | | | | |
| 3B | | | | | | |
| 3C | | | | | | |
| 4A | | | | | | |
| 4B | | | | | | |
| 4C | | | | | | |

# INTERLABORATORY STUDY 90-7: NDMA

NOVEMBER 27, 1990

REPORT DUE DATE: DECEMBER 12, 1990

IDENTIFICATION CODE:

INSTRUMENTATION: GC/TEA
INTERNAL STANDARD:
CONCENTRATION OF INTERNAL STANDARD:

| SAMPLE | RESULT (ng/L) | EXTRACTION VOLUME | FINAL VOLUME OF EXTRACT | INJECTION VOLUME | INTERNAL STANDARD (AMOUNT) | RECOVERY CHECK |
|---|---|---|---|---|---|---|
| 1A | | | | | | |
| 1B | | | | | | |
| 1C | | | | | | |
| 2A | | | | | | |
| 2B | | | | | | |
| 2C | | | | | | |
| 3A | | | | | | |
| 3B | | | | | | |
| 3C | | | | | | |
| 4A | | | | | | |
| 4B | | | | | | |
| 4C | | | | | | |

## INTERLABORATORY STUDY 90-7: NDMA

NOVEMBER 27, 1990

REPORT DUE DATE: DECEMBER 12, 1990

IDENTIFICATION CODE:

INSTRUMENTATION:

| AMPOULE | RESULTS: NATIVE (ng/L) | DEUTERATED (ng/L) | INJECTION VOLUME |
|---|---|---|---|
| NDMA STD 1 | | | |
| NDMA STD 2 | | | |
| NDMA STD 3 | | | |

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

November 27, 1990

**TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-7**

Please find enclosed two sets of twelve (12) 1000 mL amber glass bottles plus three (3) 5 mL amber ampoules. If you are missing any of the above samples or they have been broken in transit, please contact me at the above phone number immediately.

The twelve samples are to be analyzed for N-Nitrosodimethylamine (NDMA). They are labelled as follows (in duplicate):

| | | | |
|---|---|---|---|
| Effluent 1: | 1A | 1B | 1C |
| Effluent 2: | 2A | 2B | 2C |
| Effluent 3: | 3A | 3B | 3C |
| Effluent 4: | 4A | 4B | 4C |

Analysis of the samples must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 ±2 degrees Celcius **in the dark** until ready for analysis. A report form is attached. To assist in the accurate analysis of these samples, the expected level of NDMA in these samples is as follows:

For all "A" samples: <100 ppt NDMA
For all "B" samples: 300-500 ppt NDMA
for all "C" samples: 500-700 ppt NDMA

The ampoules are pure NDMA standards containing native and deuterated NDMA in dichloromethane. They are to be analyzed by direct injection and the results reported on the attached form. The ampoules are labelled as follows:

| | | | |
|---|---|---|---|
| Ampoules: | NDMA STD 1 | NDMA STD 2 | NDMA STD 3 |

To ensure that the timing of the analysts meeting is not delayed, results of the twelve samples and three ampoules are to be submitted by December 12, 1990. A report form is included with your lab identification number and the sample numbers described above.

Also to be included with the results is a copy of the official method used by the participant for the analysis of N-Nitrosodimethylamine. This information will be kept confidential for the interanalysts meeting, with summaries of the differences in procedures being tabulated for discussion purposes.

Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

December 13, 1990

**TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-7**

Thank you for your participation in Interlaboratory Study 90-7 for the analysis of N-Nitrosodimethylamine (NDMA) in effluents. As stated in the letter accompanying the samples, all participants were asked to report all results plus a copy of their official method by December 12, 1990, so as to facilitate an analysts meeting on December 18. While all of the participants reported their results within the specified timeframe, not all of the participants provided a copy of their official method. As this was a key requirement for preparing for this meeting, the December 18 meeting has been postponed until January 1991. The meeting will be scheduled as soon as I have received a copy of all of the participants official methods and everyone will be notified as soon as possible. I also requested a copy of the chromatograms/ion traces from the samples in this study. Please send me a copy of the chromatograms as soon as possible, so they may also be reviewed prior to the analysts meeting.

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

December 21, 1990

**TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-7**

Thank you for your participation in Interlaboratory Study 90-7 for the analysis of N-Nitrosodimethylamine (NDMA) in effluents. Attached are the results for the spiked effluents and the ampouled standards from all of the participants. Please review your results for any transcription errors and report them to me by January 4, 1991.

An interlaboratory analysts meeting to review the interlaboratory study results and the NDMA method, has been scheduled for all participating laboratories on:

January 8, 1991
1:00 pm
MOE Laboratory Services Branch
125 Resources Rd., Rexdale
Main Boardroom

Please confirm your attendance by January 4, 1991.

Your laboratory identification code is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842